

# Synthesis, characterisation and catalytic evaluation of iron–manganese mixed oxide pillared clay for VOC decomposition reaction

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## Abstract

A series of iron and manganese mixed oxide pillared clay with varying manganese to iron ratio has been successfully synthesized. Prepared materials were characterized by low angle XRD, TG/DTA, hydrogen TPR and nitrogen adsorption desorption experiment. All the materials were found to be thermally stable up to 500 °C having basal spacing  $\geq 16.5$  Å. Surface area and pore volume increases with the increase in the metal uptake irrespective of manganese to iron ratio. Catalytic decomposition of acetone and trichloroethylene was studied to find out the suitability of the material for VOC decomposition reaction. Catalyst (S-16/4) having high manganese content acts as better catalyst for the acetone decomposition reaction. Time on stream experiment justifies the stability of the prepared catalyst at least for 20 h with minor change in the activity. However, in case of trichloroethylene (TCE) decomposition catalyst (S-8/12) with higher iron content shows better activity. Quick deactivation of the catalyst for TCE decomposition is noticed for all the prepared materials.

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**Keywords:** Iron and manganese mixed oxide; Pillared clay; Decomposition; Acetone and trichloroethylene

## 1. Introduction

Several methods [1] are in use for the removal of industrial organic air effluents. Among them the most commonly employed methods are adsorption [2] and high temperature incineration [3]. However, both the methods have some disadvantages and hence there is a need to find out an efficient method to tackle the growing environmental problems. In this context catalytic combustion of organic pollutants offers considerable advantages over the industrially operated thermal combustion process. Generally, oxidative destruction is possible at low temperature in presence of a catalyst and hence it is not classified as an incineration process. In addition catalytic process is more energy efficient and can operate with very dilute pollutants.

A number of catalyst has been used for the complete oxidation of VOCs, which broadly comes under two categories: supported noble metals (Pt, Pd etc.) [4] and oxide of the transition metals [5–7]. However, both categories of catalysts

have advantages and disadvantages. In addition to the single oxide systems some mixed oxide having perovskite structure  $\text{LaMnO}_3$  [8] or  $\text{La}_{1-x}\text{Ca}_x\text{FeO}_3$  [9] have also found effective as catalyst for decomposition of different volatile organic compounds. In some cases noble metals along with transition metal oxides have been used as an effective catalyst with synergetic effects [10].

Among transition metal oxide mostly manganese oxide of different polymorphs [11–13], perovskite type manganites [14], manganese oxide supported on alumina [15] and titania [16,17] have been proposed as cheap, environment friendly, active and stable catalyst. In addition some iron oxide and supported iron oxides were found to be active catalysts [18]. Even manganese nodule containing mostly manganese oxide and iron oxide as active components was found to be efficient for the VOC decomposition reaction [19]. However, very little attention has been paid to the choice of support material for low temperature application [5,6,20]. Till date mostly  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2\text{--SiO}_2$  [5,6,21–23] have been studied as possible support. It is understood that mostly Bronsted acidity with redox sites and high surface area are contributing factor for better catalytic performance.

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Pillared clays are one of the most widely studied families among the new group of high surface area microporous materials developed. Beauty of these materials lies in the capacity of intercalating different active oxide species inside the clay layers. Recent advances in the synthesis of pillared clay have expanded considerably the scope of their potential catalytic applications. As a result there is now a renewed interest in the pillared material as polyfunctional catalysts and catalyst supports [24]. In this context clays as support and transition metal pillared clays as catalyst are also good option due to the presence of both redox and acid sites. However, till date exploration of these materials is very limited in the literature [25–28]. Transition metal oxide supported alumina pillared clay [26], zirconia pillared clay [27] were studied recently as effective catalyst for the decomposition of chlorocompounds. Complete oxidation of acetone on manganese oxide supported pillared clay justifies the importance of clay as support and manganese oxide as active catalyst [28]. Particularly in case of pillared clay, dispersion of active oxide phase and the acidity involved in the clay plays an important role because of their participation in the decomposition reaction [29]. Though manganese and iron oxides are active catalyst [18,28] for the decomposition of VOCs, till date there is no report on the synthesis of the said mixed oxide pillared clay. Hence it is of interest to intercalate both iron and manganese oxide in different ratio inside the clay layers as active species.

Therefore, the present paper deals with the synthesis characterisation and catalytic evaluation of novel manganese and iron mixed oxide pillared clay with varying manganese to iron ratio towards the decomposition of acetone and trichloroethylene.

## 2. Experimental

### 2.1. Material synthesis

Sodium exchanged montmorillonite of Mainburg area, Germany having the ion-exchange capacity of 85 meq/100 g and surface area of 85 m<sup>2</sup>/g was used as the starting material for the pillared clay preparation. Non aqueous solution of trinuclear acetate complexes of iron(III) and manganese(III) were used as precursors. Both the complexes were prepared according to the reported methods [29,30] and used as such. In this experiment total metal complex to clay ratio was maintained at 20 mmol/g varying the Mn(III) to Fe(III) ratio from 20/0 to 4/16. Ion exchange was carried out at room temperature in stirring condition for 4 h. All the five samples were filtered, washed with methanol and dried at 30 °C for further use. The samples are denoted as S-A/B, where A and B are the molar ratio of Mn(III) to Fe(III) in the solution during ion exchange. Obtained materials were dried at 100 °C. Subsequently materials were heated in air for 4 h at 300 and 500 °C for further use.

### 2.2. Estimation of iron and manganese in the samples

The amount of iron and manganese present in the diluted solution was estimated by AAS (Chemito-203) after acid dissolution of the prepared materials.

### 2.3. XRD analysis

Low angle XRD patterns of the clay samples oriented on glass slides were recorded on a Philips semiautomatic diffractometer with Ni filter using Cu K<sub>α</sub> radiation from 2θ = 2 to 20°. Basal spacing was calculated from *d*<sub>001</sub> value.

### 2.4. Surface area measurement

Surface area (BET) was determined by nitrogen adsorption desorption method at liquid nitrogen temperature using Quantasorb (Quantachrome, USA). Prior to the measurement, all the samples were degassed at 150 °C at 10<sup>−3</sup> Torr for 5 h.

### 2.5. TG/DTA

TG-DTA analysis of the 30 °C dried samples were carried out in dry air using a Shimadzu DT-40 thermal analyser in the range of 30–600 °C at a heating rate of 20 °C/min.

### 2.6. Hydrogen TPR

Hydrogen TPR was performed with help of CHEMBET-3000 (Quantachrome, USA) instrument in the temperature range of 40–800 °C. About 0.1 g of powdered sample was taken inside a quartz “U” tube and degassed at 400 °C for 1 h with ultra pure helium gas. After cooling the sample to room temperature H<sub>2</sub> gas of 1000 ppm with N<sub>2</sub> gas was flowed through the sample maintaining a heating rate of 10 °C/min to record the profile. A pure mixed oxide material was prepared from the mixture of the used complexes with Mn to Fe ratio of 12:8 and preheated at 500 °C for 4 h before TPR study.

### 2.7. Catalytic activity

Acetone and trichloroethylene decomposition reaction over all the prepared 500 °C preheated samples were performed in a fixed bed catalytic reactor (10 mm diameter) using 0.1 g of catalyst with on line GC. Prior to the reaction study all the catalysts were preheated at 300 °C and 400 °C for acetone and TCE decomposition study respectively in nitrogen atmosphere for 1 h. Reactant was quantitatively (5 ml/h) supplied to the reactor from a continuous micro-feeder (Orion, USA) through a vapouriser using nitrogen as the carrier gas having flow rate of 20–60 cc/min. The amount of acetone and trichloroethylene passed over the catalyst was estimated by GC to be 550–500 and 300–350 ppm, respectively. All the connections from reactor to the GC were heated at 120 °C by heating tape to avoid condensation of the reactant or the liquid products inside the apparatus. Reaction products were analysed by means of on line GC (Simadzu-17A) in FID mode using capillary columns. Amount of CO<sub>2</sub> was estimated in TCD mode.

### 3. Result and discussion

#### 3.1. Intercalation

Prepared manganese complex is unstable in aqueous solution but stable in both methanol and glacial acetic acid. However, methanol was used as solvent in this study due to the low uptake of Mn(III) complex from glacial acetic acid [31]. Preliminary study showed that uptake increases with the increase in the total metal ion to clay ratio up to 20 mmol/g and hence all the study was performed at that ratio. Uptake of both the complexes from the mixed solution shows an interesting pattern as presented in Fig. 1. In all the cases, Fe(III) uptake is quite higher in comparison to that of Mn(III) complex though the molecular size and charges are mostly same for both the complexes. In particular, when manganese to iron molar ratio is 10/10 in the solution, iron uptake is nearly two times higher than that of manganese (Table 1). Of course similar trend of high iron(III) uptake was also observed in case of Fe(III) and Cr(III) mixed pillared clay synthesis [32]. In addition total metal uptake increases with the increase in the iron(III) ratio in the solution. This indicates a high affinity of the clay layer towards trinuclear iron(III) acetate complex.

#### 3.2. Textural properties

Basal spacing of the pillared material mostly increases with the increasing total metal intercalation irrespective of iron to manganese ratio. Though the difference is small, the highest basal spacing and metal uptake is observed with S-4/16 material. All the prepared materials are found to be stable up to 500 °C with appreciable basal spacing. More over after ethylene glycol adsorption nearly same interlayer distance was observed, indicating that the stabilization of the oxide pillars is due to the strong complex to clay interactions.

In the DTA thermograms (Fig. 2A and B), only one exothermic peak is observed between 260 and 315 °C, corresponding to the decomposition of acetyl group of the complexes. However, both the pure complexes decomposes in a sharp range of 245–260 °C in air [31,33]. Probably the partial bonding of the clay hinders the decomposition resulting in a broad exothermic peak at higher temperature.

#### 3.3. Surface properties

Table 2 shows the increase in surface area and pore volume with the increasing calcination temperature up to 500 °C.

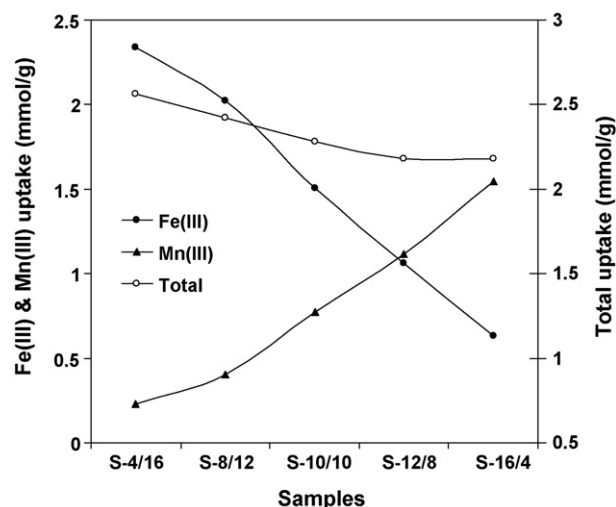


Fig. 1. Variation in uptake of Mn(III) and Fe(III) acetato complexes by Na-montmorillonite with the change in manganese to iron ratio in the solution.

Among all the prepared sample surface area and the basal spacing increases with the increasing metal uptake at all calcination temperature. Assuming the pores to be cylindrical, the average pore diameter was calculated using the formula  $D_{av} = 4V_p/S_p$ , where  $V_p$  is the pore volume and  $S_p$  is the total internal surface area of the pores. From the Table 2, it is clear that with the increase in calcination temperature,  $D_{av}$  decreases for all the prepared materials. Again specific surface area  $S_{\alpha}$  calculated from the  $\alpha_s$  plots are found to be very close to the  $S_{BET}$  values, indicating the accuracy of the reference method. S-4/16 shows highest surface area and pore volume among all the prepared materials, though the difference is very small.

#### 3.4. TPR study

TPR of all the studied pillared samples showed the similar pattern (Fig. 3) with the change in intensity only. In all the TPR profiles of prepared samples prominent peaks at 350, 460 and 708 °C and a small shoulder at 265 °C were observed. Peak at 350 °C mostly corresponds to the reduction of  $MnO_2$  and  $Mn_2O_3$  to  $Mn_3O_4$  which subsequently reduced to  $MnO$  in the second steps at 460 °C [27]. In most of the cases the intensity of the second peak is more than the first one indicating the formation of  $Mn_3O_4$  with  $MnO_2/Mn_2O_3$  inside the clay layer during calcination. Many studies have reported earlier that  $FeO$  is observed in the reduction process on the supported catalyst within 350–570 °C. However, in our study it is difficult to

Table 1

Variation in Mn(III) and Fe(III) uptake due to the change in manganese to iron ratio in the mixed complexes solution

Samples	Mn:Fe molar ratio in solution	Mn intercalated (wt%)	Fe intercalated (wt%)	Mn + Fe intercalated (wt%)	Mn:Fe intercalated
S-16/4	16:4	7.82	3.42	11.24	2.287
S-12/8	12:8	5.78	5.61	11.39	1.03
S-10/10	10:10	4.08	7.75	11.73	0.526
S-8/12	8:12	2.15	10.14	12.29	0.212
S-4/16	4:16	1.23	11.54	12.77	0.107

Table 2

Textural properties including average pore diameter ( $D_{av}$ ), micropore volume ( $V_m$ ) and surface area ( $S_a$ ) calculated from  $\alpha_s$  method of prepared materials

Sample	Basal spacing (Å)		Pore volume (cm <sup>3</sup> /g)		Surface area (m <sup>2</sup> /g)			$S$ (m <sup>2</sup> /g)		$V_m$ (cm <sup>3</sup> /g)		$D_{av}$ (Å)	
	300 °C	500 °C	300 °C	500 °C	300 °C	400 °C	500 °C	300 °C	500 °C	300 °C	500 °C	300 °C	500 °C
S-16/4	17.0	16.5	0.2154	0.2217	238	259	268	235	269	0.105	0.146	37.8	33.3
S-12/8	17.0	16.6	0.2158	0.2238	243	265	272	239	274	0.105	0.145	39.7	33.6
S-10/10	17.1	16.6	0.2183	0.2243	243	269	277	238	273	0.107	0.147	40.2	35.4
S-8/12	17.2	16.8	0.2192	0.2292	246	273	282	244	277	0.111	0.148	39.7	35.2
S-4/16	17.3	16.9	0.2213	0.2346	251	274	286	248	282	0.114	0.151	37.8	34.1

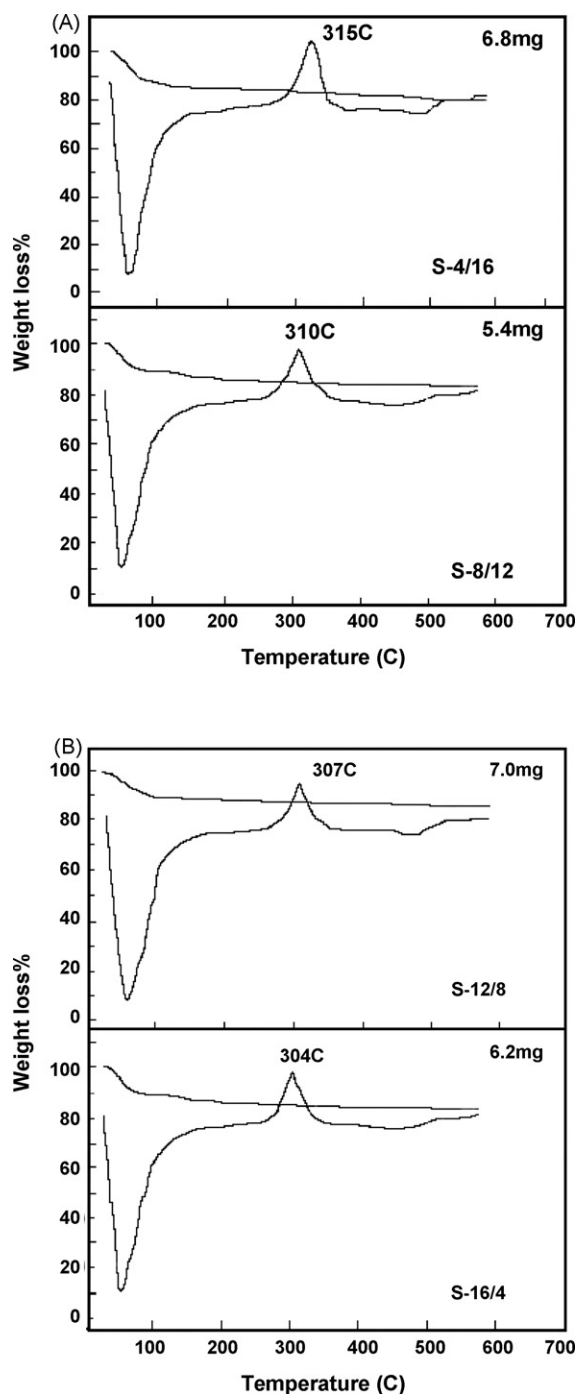


Fig. 2. (A) Thermal analysis of manganese and iron mixed pillared clays. (B) Thermal analysis of manganese and iron mixed pillared clays.

indicate the formation of FeO in the process due to overlapping of peaks in the said region. However, the clear peak at 708 °C is due to the conversion of iron oxide to Fe<sup>0</sup> as the pure clay containing 3.1% iron also showed a similar peak. Intensity of the peak increases with the increase in iron content of the sample. However, a little shifting of reduction peaks towards higher temperature was observed for the pillared clay in comparison to that of pure oxides (Fig. 3) which may be due to the restriction of the clay layers.

### 3.5. Acetone decomposition

The acetone conversion with respect to reaction temperature plotted in Fig. 4 was calculated from the estimation of remaining acetone after reaction. In addition acetone conversion was also estimated from CO<sub>2</sub> formed (Table 3) as a

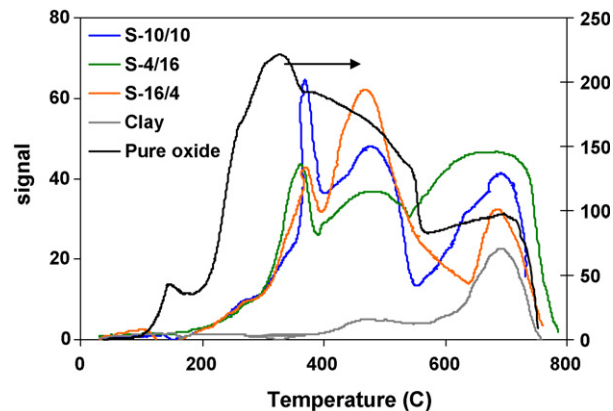


Fig. 3. Hydrogen TPR profile of different pillared and pure clays.

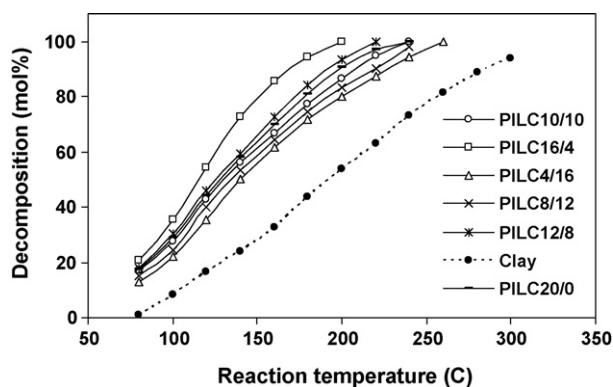


Fig. 4. Acetone conversion over prepared catalysts at different temperatures.

Table 3

Acetone conversion at different temperatures estimated by two different methods

Catalysts	Reaction temperature		
	100 °C	160 °C	200 °C
Clay	8.3 (7.8)	32.7 (26.6)	53.8 (44.6)
S-4/16	22.7 (22.2)	62.9 (62.1)	79.9 (78.5)
S-8/12	24.6 (23.9)	65.3 (64.5)	83.1 (81.8)
S-10/10	28.2 (27.7)	67.4 (66.7)	86.4 (85.4)
S-12/8	30.3 (29.6)	72.7 (71.9)	93.5 (92.6)
S-16/4	35.3 (34.5)	85.4 (84.6)	100 (99.3)

Data in the parenthesis is calculated from CO<sub>2</sub> estimation.

product. Most of the cases of pillared clay variation in both the results is quite small. This indicates that most of the acetone decomposes to CO<sub>2</sub> in air without forming any major side products in the temperature range of 200–260 °C. However, the difference in both the results increases with the increase in iron content in the sample. Interestingly, in case of pure clay the discrepancy is much more which indicates the formation of some side product thus decreasing the CO<sub>2</sub> content. It was earlier reported that some stable polymeric species can be formed over acidic catalyst through enolate ion formation from acetone [34] instead of decomposing to CO<sub>2</sub>. As the Bronsted acidity of clay is quite high in comparison to that of iron and manganese mixed oxide pillared clay so the probability of polymeric formation increases in case of the pure clay. There are relatively few reports on the complete decomposition of acetone over various catalysts. Complete decomposition of 600 ppmv acetone over several Mn/γ-Al<sub>2</sub>O<sub>3</sub> and Mn/SiO<sub>2</sub> catalyst was reported in the temperature range of 247–307 °C [35]. Even complete oxidation of acetone in air over α-Mn<sub>2</sub>O<sub>3</sub> and δ-Mn<sub>2</sub>O<sub>3</sub> was reported in the temperature range of 257–317 °C [36] and 235 °C [19] respectively with a flow rate of 100 ml/min. Interestingly, in the present study prepared iron–manganese mixed oxide pillared clay decomposes 550 ppmv acetone at a flow rate of 60 ml/min relatively at lower temperature which may be due to the presence of Mn<sub>3</sub>O<sub>4</sub> in addition to Mn<sub>2</sub>O<sub>3</sub> in our material as indicated in the TPR profile. Out of all the prepared materials S-16/4 shows complete oxidation of acetone at lowest temperature. As the clay itself contain 3.1 wt% of Fe, so the manganese to iron ratio is 1.2 in the above said material. When compared with the pillared clays, catalytic decomposition of acetone is quite low in case of pure clay. This clearly indicates that the increased surface area and the presence of mixed oxide pillars are important for the acetone decomposition reaction.

A series of catalytic runs were performed at constant temperature of 200 °C to observe the stability of the prepared materials during the reaction. It is well observed (Fig. 5) that all the catalysts show a noticeable increase of acetone conversion during the first 2 h of reaction and then decreases slowly depending on the catalyst material. Similar trend was also reported with pillared clay catalysts [26]. In particular the decrease in acetone conversion with time on stream is more prominent with the increase in the iron content of the catalyst. Above all time on stream experiment showed that the prepared

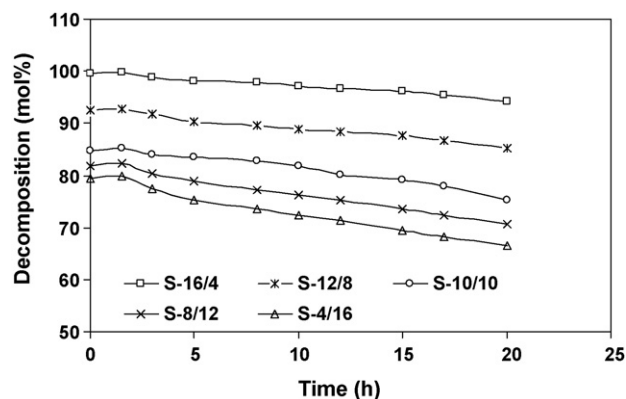


Fig. 5. Time on stream experiment of acetone conversion over different catalysts at 200 °C.

pillared clay material can be effectively used as decomposition catalyst without much change in the activity at least for 20 h.

### 3.6. Decomposition of trichloroethylene (TCE)

Oxidation of trichloroethylene in air over all the prepared catalysts was presented in the Fig. 6. It is well visible that the catalytic activity of the pillared material is quite high in comparison to that of pure clay at all temperatures. The catalytic activity increases with the increase in iron content in the pillars up to 10.14 wt% which is different from the acetone decomposition activity. It is well understood that the reactivity of Cl-VOC is different to that of non chlorinated VOCs due to the high electronegativity of chlorine. On the other hand, chlorine has a lone pair of electrons to interact thus leading to the formation of chemical bonds with adjacent atoms [37]. Probably due to the high electronegativity of TCE reaction with iron oxide is more effective. TCE decomposition increases with increase in the iron content of the catalyst up to 10.14 (S-8/12) and then decreases. With the pure iron oxide pillared clay activity is less than the sample S-8/12 which indicates the importance of manganese oxide in the pillars for TCE decomposition reaction. However, the time on stream experiment (Fig. 7) shows the quick deactivation of the catalyst. In particular with the increase in the iron content rate of deactivation also increases. In this context performance of

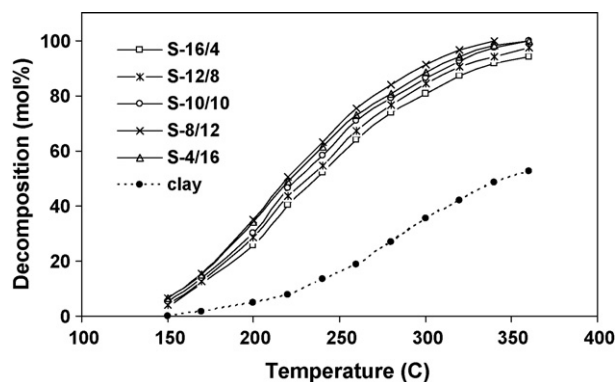


Fig. 6. Trichloroethylene conversion over different catalysts calcined at 500 °C.



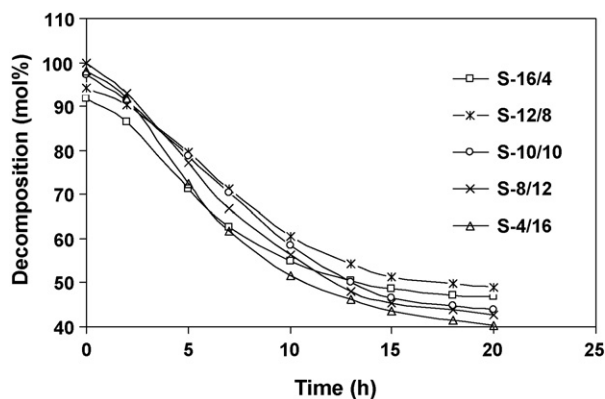


Fig. 7. Time on stream experiment of trichloroethylene conversion at 340 °C.

low iron content sample (S-12/8) is better. During the reaction HCl was formed which was detected with the products. It is well known that HCl can react with the iron oxide containing catalyst which will lead to the leaching of the iron from the materials [38]. Probably, the catalyst deactivates quickly due to the structural damage caused by the HCl. It is observed that the surface area of the catalyst decreases to 108 m<sup>2</sup>/g after 8 h of reaction from 282 m<sup>2</sup>/g. This decrease in surface area again supports the partial degradation of porous structure during reaction. From Fig. 8 it is well visible that TCE decomposition activity increases with the increase in surface area and iron content of the pillars up to S-8/12 and then decreases. As a whole the quick deactivation of the catalyst is the major concern particularly for the decomposition of chloro compounds. However, similar deactivation was reported with iron containing zeolite and red mud catalysts [18].

### 3.7. Effect of iron to manganese ratio on the catalytic activity

Manganese to iron ratio in the material plays an important role in the acetone decomposition reaction. In particular, with the decrease in iron content of the catalyst catalytic activity increases up to sample S-16/4. In case of pure manganese pillared clay catalytic activity decreases (Fig. 4) though it contains 3.1 wt% iron thus justifying the importance of iron oxide with the manganese oxide in the pillars for acetone

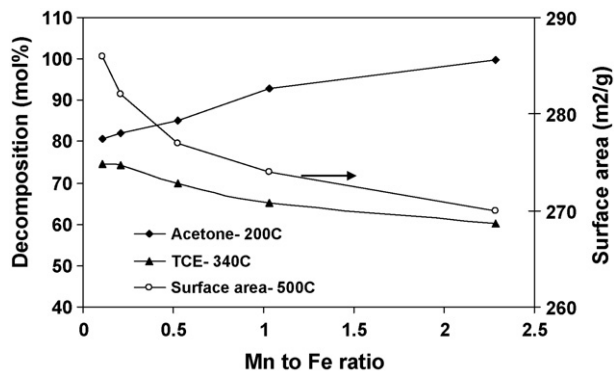


Fig. 8. Effect of manganese to iron ratio of the catalyst calcined at 500 °C on catalytic activity and surface area.

decomposition reaction. Therefore presence of iron with the manganese oxide in the pillar is crucial for the better catalytic activity. However, the participation of all the iron present in the clay itself in the catalytic reaction is doubtful as all the iron present in the clay layers may not be accessible to the reactants. It is understood from the earlier report that manganese supported systems show better catalytic activity than the pure manganese oxide systems [27]. Present study also showed the importance of both oxide systems in certain ratio with the clay as support for the improved catalytic activity for acetone decomposition reaction.

It is again well observed that iron to manganese ratio plays an important role in the overall catalytic activity for the decomposition of TCE. However, decomposition activity increases with the increase in iron content of the pillar up to S-8/12 and thereafter decreases. In this case sample S-8/12 having manganese to iron ratio of 0.212 shows maximum catalytic activity at lowest temperature. From the above study it is clear that both the decomposition reactions are much more dependent on the manganese to iron ratio in the pillar rather than the surface area and pore volume of the catalyst. Therefore, it can be concluded that manganese and iron mixed pillared clay can be used as potential decomposition catalyst. In particular, different manganese to iron ratio can be selected depending on the type of reactants.

## 4. Conclusions

Present paper reports the successful preparation of thermally stable manganese–iron mixed oxide pillared clay. It is possible to vary the manganese to iron ratio in the pillars by varying the iron(III) to manganese(III) complex ratio in the solution. Pillared material (S-16/4) having high manganese content is found to be the best catalyst for the acetone decomposition reaction. It can be concluded that the presence of small amount of iron oxide in the pillar is essential for improved catalytic activity. Complete decomposition of acetone is feasible at lowest temperature of 200 °C over the prepared pillared clay (S-16/4). Above material also performed well in the time on stream experiment and hence can be utilized for the acetone decomposition reaction. On the other hand, material (S-8/12) with high iron contents acts as a better catalyst for TCE decomposition. However, quick deactivation of the catalyst for TCE decomposition reaction is the major concern for future use particularly for VOC containing chloro-compounds. It is believed that the evolved HCl mostly reacts with the pillared materials thus decreasing the activity. As a whole the prepared manganese and iron mixed oxide pillared materials can be used as an efficient decomposition catalyst particularly for the non chloro compounds.

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